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Phase Separation in Polymer Solutions from a Born-Green-Yvon Lattice Theory [1]

J. Luettmer-Strathmann and J. E. G. Lipson
Department of Chemistry
Dartmouth College, Hanover, NH 03755

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Abstract

Phase separation in mixtures of polymers and alkanes is investigated with the aid of a recently developed lattice model, based on the Born-Green-Yvon (BGY) integral equation approach to fluids. The system-dependent parameters of the BGY lattice model for binary mixtures are deduced from those of its pure components, which in turn are determined from a comparison with experimental data. The lower critical solution temperatures (LCST's) for polyethylene in various n-alkanes were predicted from the BGY lattice model and compared with experimental data. While the model underestimates the LCST's for the smaller alkanes it reproduces the experimental values very well for the higher alkanes (decane through tridecane). The effect of the chain length of the polymer on the solubility is investigated for the case of decane as a solvent.

Introduction

In many polymer/solvent systems, phase separation occurs at a lower critical solution temperature (LCST) [1]. For temperatures smaller than the LCST the polymer is soluble while a miscibility gap opens above the LCST which is closed again at an upper critical solution temperature (UCST). These lower critical solution temperatures are difficult to predict accurately from theory [2, 3, 4]. In this work, we employ a recently developed lattice model [5, 6, 7, 8] based on the Born-Green-Yvon (BGY) integral equation approach to fluids to investigate the miscibility of polyethylene in alkanes. The BGY lattice model provides a compact expression for the configurational part of the Helmholtz free-energy density which allows the calculation of the relevant thermodynamic properties of a mixture. In addition to the system-dependent parameters of the pure components, the lattice model for a binary mixture contains an energy parameter describing interactions between unlike molecules. In this work the interaction energy is approximated by the geometric mean of the energy parameters of the pure components, allowing the thermodynamic properties of the mixture to be predicted from those of the pure components. In the following sections we describe how the BGY lattice model is used to predict the LCST's and corresponding coexistence curves for polyethylene in various alkanes, and then compare our results with experimental data.

Born-Green-Yvon lattice model for fluids

In the BGY lattice model, a molecule of species i is assumed to occupy r_i contiguous sites on a lattice having coordination number z and a total of N_0 lattice sites. As in earlier work [7, 8], we set $z = 6$. The site-fraction ϕ_i is defined as $\phi_i = r_i N_i / N_0$, where N_i is the number of molecules of component i while $\phi_\mathrm{h} = N_\mathrm{h}/N_0$ is the fraction of empty sites or holes, where N_h is the number of holes. Each molecule of species i has $q_i z = r_i(z-2) + 2$ interaction sites, leading to the definition of concentration variables $\xi_i = q_i N_i / (N_\mathrm{h} + \sum_j q_j N_j)$ and $\xi_\mathrm{h} = N_\mathrm{h}/(N_\mathrm{h} + \sum_j q_j N_j)$ which account for the nearest-neighbor connectivity of the molecules. The interaction energy associated with nonbonded nearest neighbors of the same species is ϵ_{ii}, while ϵ_{ij} corresponds to interactions between unlike nearest neighbor segments. Using the Born-Green-Yvon integral equation approach, Lipson [5, 6] derived an expression for the dimensionless configurational Helmholtz free energy per lattice site $\hat{a} = \beta A / N_0$ of an M-component mixture

$$\hat{a} = \frac{\beta A}{N_0} = \sum_{i=\mathrm{h},1}^{M} \left(\frac{\phi_i}{r_i} \ln \phi_i + \frac{q_i z \phi_i}{2 r_i} \left\{ \ln \left[\frac{\xi_i}{\phi_i} \right] - \ln \left[\xi_\mathrm{h} + \sum_{j=1}^{M} \xi_j \exp(-\beta \epsilon_{ij}) \right] \right\} \right), \quad (1)$$

where $\beta = 1/(k_\mathrm{B} T)$, T is the temperature and k_B is Boltzmann's constant. Denoting the total volume of the lattice by $V = v N_0$, where v is the volume per site, we obtain the Helmholtz free-energy density A/VT

$$A/VT = k_\mathrm{B} \hat{a}/v + a_0, \quad (2)$$

where a_0 is a caloric background which is not discussed further in this work. All thermodynamic properties of a mixture can now be derived from the thermodynamic relation

$$d(A/VT) = (U/V) d(1/T) + \sum_{j=1}^{M} (\mu_j/T) d(\rho_j), \quad (3)$$

where U is the internal energy of the system, and where $\rho_j = N_j/V = \phi_j / r_j v$ and μ_j are the number density and chemical potential of component j, respectively. The pressure P and the chemical potentials μ_i, for example, are given by

$$P = -\frac{1}{\beta v} \left[\hat{a} - \sum_{j=1}^{M} \phi_j \left(\frac{\partial \hat{a}}{\partial \phi_j} \right)_{\beta, \phi_{k \neq j}} \right], \qquad \mu_i = \frac{r_i}{\beta} \left(\frac{\partial \hat{a}}{\partial \phi_i} \right)_{\beta, \phi_{k \neq i}}. \quad (4)$$

It now becomes convenient to focus on molar quantities, so that ρ_j becomes the molar density of component j, v denotes the volume of a mole of lattice sites, the energy parameters ϵ are measured in J/mol, and k_B is replaced by the universal gas constant R.

Application to one-component fluids

For the case of a one-component fluid, equations (1)–(4) are evaluated with $M = 1$, so that we can drop the subscripts other than h. There are three system-dependent parameters which we determine from a comparison with experimental data: the number r of lattice sites occupied by a single molecule, the volume v per mole of sites, and the interaction energy ϵ.

To obtain parameters for the n-alkanes from pentane through tridecane we considered coexistence densities. The critical temperature T_c and the critical density ρ_c of a one-component fluid are determined by the following two conditions:

$$\left(\frac{\partial\mu}{\partial\rho}\right)_T = 0, \qquad \left(\frac{\partial^2\mu}{\partial\rho^2}\right)_T = 0, \tag{5}$$

For temperatures T smaller than T_c the coexistence densities ρ_vap and ρ_liq can be found from the conditions that pressure and chemical potential are equal in the vapor and the liquid phase, i.e.

$$P(T, \rho_\mathrm{vap}) = P(T, \rho_\mathrm{liq}), \qquad \mu(T, \rho_\mathrm{vap}) = \mu(T, \rho_\mathrm{liq}). \tag{6}$$

We determined the parameters r, v, and ϵ for a number of n-alkanes between methane and octane by comparing calculated liquid and vapor densities for temperatures between $0.5T_\mathrm{c}$ and $0.9T_\mathrm{c}$ (to avoid the critical region) with values tabulated by Vargaftik [9]. We then correlated the parameters with the chain length n of the alkanes, where we typically excluded the results for the lowest alkanes. The resulting expressions for the parameters as a function of chain length are given by

$$rv/(\mathrm{L/mol}) = 0.016n + 0.015, \tag{7}$$

$$r\epsilon/(\mathrm{J/mol}) = -2150n - 3150, \tag{8}$$

$$\sqrt{r} = -0.877539 + 1.512447\sqrt{n + 1.4651}\left(\frac{1}{\sqrt{n}} + 0.58259\right). \tag{9}$$

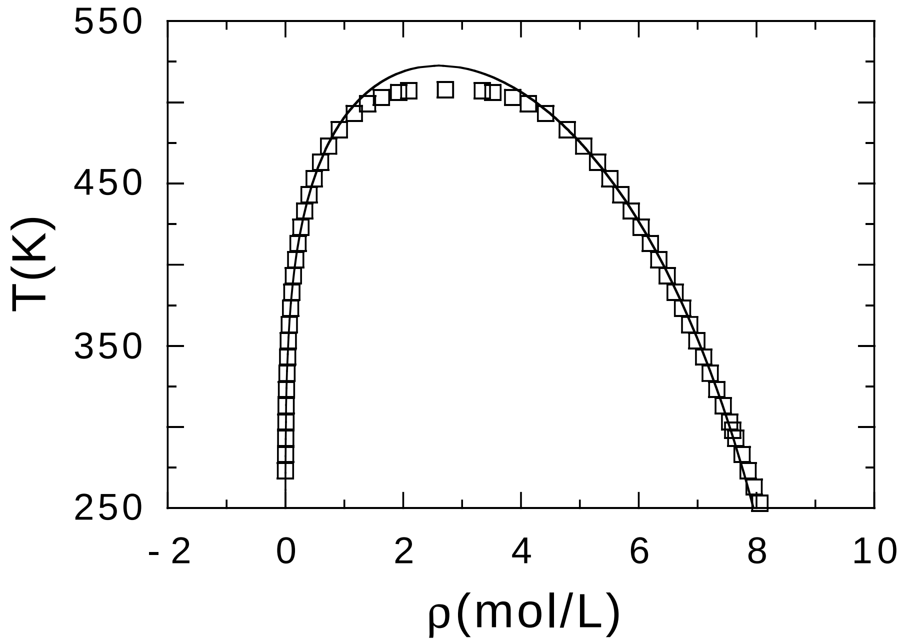

Figure 1: The coexisting vapor and liquid densities for n-hexane. The symbols indicate values from Ref. [9], the solid line values calculated from Eqs. (6) with system-dependent parameters given in Table 1.

The first of these equations, Eq. (7), reflects the fact that the hard core volume of the alkanes is expected to grow linearly with chain length, while Eq. (8) conveys a linear relationship between the interaction energy per mole and the chain length n. Due to end effects, neither relation is expected to hold for very small n. The last equation, Eq. (9), is motivated by the variation of the experimental [10] and calculated critical temperatures of the alkanes with chain length. In Table 1 we present the values of the system-dependent parameters for pentane through tridecane according to Eqs. (7)–(9). Calculated values for the coexistence densities of hexane along with values from Ref. [9] are presented in Fig. 1, while percent deviations between calculated and tabulated values for all alkanes considered in this work are presented in Fig. 2. The highest deviations seen in Fig. 2 are for vapor densities and are, in part, a result of the correlation of the parameters with chain length. The two figures show that our model gives a reasonable description of the coexistence densities outside the critical region.

System-dependent parameters for polyethylene (PE) were determined from a com-

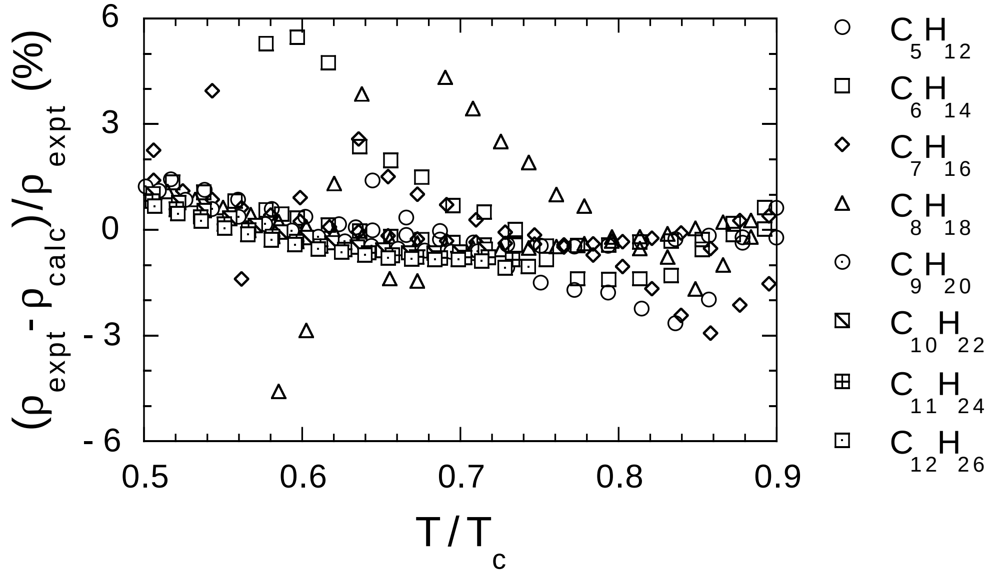

Figure 2: Percent deviations between values for the coexistence densities as provided in Ref. [9] and as calculated from Eqs. (6) with system-dependent parameters given in Table 1.

Table 1: System-dependent parameters for the pure components.

name	molmass	r	v (mL/mol)	ϵ (J/mol)	LCST(K)
n-Pentane	72.146	9.505229	9.994499	-1462.353	260.4
n-Hexane	86.172	10.35107	10.72353	-1550.565	371.2
n-Heptane	100.198	11.22030	11.31877	-1622.060	435.9
n-Octane	114.224	12.10191	11.81632	-1681.552	484.0
n-Nonane	128.250	12.99011	12.24009	-1732.088	522.8
n-Decane	142.276	13.88162	12.60660	-1775.729	555.5
n-Undecane	156.302	14.77453	12.92766	-1813.933	583.7
n-Dodecane	170.328	15.66765	13.21193	-1847.756	608.6
n-Tridecane	184.354	16.56028	13.46595	-1877.987	630.8
PE	140262.0	15890.72	9.621464	-1988.320	
PE	85000.0	9629.90	9.621934	-1988.458	
PE	50000.0	5663.81	9.623040	-1988.729	

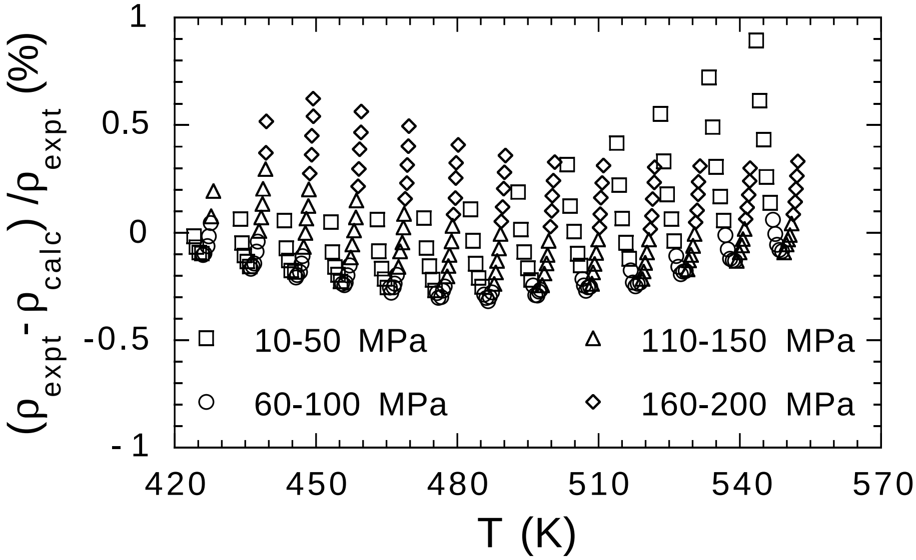

Figure 3: Percent deviations between experimental [11, 12] and calculated (cf. Eq. (4)) values of the densities of polyethylene at given temperature and pressure.

parison with experimental PVT data [11, 12] in the liquid region for temperatures between 420K and 560K and pressures between 10MPa and 200MPa. When the density of a long chain polymer is given as a mass density, rather than a number density, the pressure is expected to be independent of the molecular mass [11, 12] of the polymer. We determined system-dependent parameters for PE from a comparison between experimental and calculated pressures using three different molecular masses for the polymer. The representation of the experimental data was virtually identical in the three cases. and the resulting values for the parameters, as presented in Table 1, show that for long chain polymers ϵ and v are indeed independent of the molecular mass, while r is proportional to it. A comparison between calculated and experimental values for the density at given temperature and pressure is presented in Fig 3. The deviations are generally smaller than 0.3% but reach up to 1% for the lowest pressures.

Phase separation in binary solutions

To discuss phase separation in binary mixtures, it is convenient to introduce the total molar density $\rho = \rho_1 + \rho_2$ and the mole fraction $x = \rho_2/\rho$ of component 2. The thermodynamic field conjugate to the mole fraction x is the difference of the chemical potentials $\mu = \mu_2 - \mu_1$. In terms of these variables, the conditions for a point T_c, P_c, x_c on the critical line of a binary mixture take the form [13]:

$$\left(\frac{\partial\mu}{\partial x}\right)_{T,P} = \left(\frac{\partial\mu}{\partial x}\right)_{T,\rho} - \rho^2\left(\frac{\partial\mu}{\partial\rho}\right)^2_{T,x}\Big/\left(\frac{\partial P}{\partial\rho}\right)_{T,x} = 0, \tag{10}$$

$$\left(\frac{\partial^2\mu}{\partial x^2}\right)_{T,P} = 0. \tag{11}$$

The first of the two equations defines the spinodal while the second one implies that, for given pressure, the critical point is an extremum of the spinodal in the T-x plane. Hence, lower and upper critical solution temperatures (LCST's and UCST's) correspond to the minimum and maximum of their spinodals, respectively. For temperatures $LCST < T < UCST$, the mixture phase separates into two phases of different mole fractions x_I and x_{II}. For a given pressure P, the coexisting phases satisfy

$$\mu(T,P,x_I) = \mu(T,P,x_{II}), \qquad \mu_1(T,P,x_I) = \mu_1(T,P,x_{II}). \tag{12}$$

For typical solutions of polymers in alkanes, the mole fractions x are very small numbers so that it is more convenient to employ mass fractions c:

$$c = M_2x/(M_2x + M_1(1-x)), \tag{13}$$

where M_1 and M_2 are the molecular masses of component 1 and 2, respectively.

When the BGY lattice model is applied to binary mixtures, Eqns. (1)–(4) are evaluated with $M = 2$. The total molar density $\rho = \rho_1 + \rho_2$ and the mole fraction $x = \rho_2/\rho$ of the mixture are related to the site fractions ϕ_1 and ϕ_2 by

$$\rho = \frac{1}{v}\left(\frac{\phi_1}{r_1} + \frac{\phi_2}{r_2}\right), \qquad \frac{1}{x} = 1 + \frac{\phi_1}{r_1}\frac{r_2}{\phi_2}. \tag{14}$$

In addition to the energy parameters $\epsilon_{11} \equiv \epsilon_1$ and $\epsilon_{22} \equiv \epsilon_2$, and the numbers of segments r_1 and r_2, which are determined directly by the pure components of the mixture, values need to be supplied for the interaction energy ϵ_{12} and the volume v of

a mole of lattice sites. For the energy parameter ϵ_{12} we employ Berthelot's geometrical mean combining rule [13]:

$$\epsilon_{12} \equiv -\sqrt{\epsilon_1 \epsilon_2}. \tag{15}$$

To find a value for v, we take advantage of the fact that the BGY model for the pure polymer depends more strongly on the product rv than on the values of the number of segments r and the volume v separately. Hence, for a mixture of an alkane and polyethylene, we assign the value v_1 of the alkane to the mixture, and rescale the segment length of the polymer, i.e.

$$v \equiv v_1, \qquad r_2 \rightarrow (r_2 v_2)/v_1. \tag{16}$$

When parameters v and r_2, given by Eq. (16), are used to compare experimental and calculated PVT data for pure polyethylene over the whole temperature and pressure range, it is seen that the new parameters diminish the overall agreement between experiment and theory. However, for the lowest pressures the description of the PVT surface is improved over that using the original parameters, and becomes excellent for the highest alkanes. This is important since we are going to investigate phase separation of polyethylene solutions at *atmospheric* pressure.

To determine the lower critical solution temperatures for mixtures of polyethylene and the various alkanes discussed in the previous section, we employed the parameters presented in Table 1, where the highest molecular-mass parameters were used for polyethylene, together with Eqs. (15) and (16). We then solved Eqn. (10) numerically to find the spinodal curve for atmospheric pressure $P = 0.1$MPa. The LCST was identified as the minimum of the spinodal curve as a function of x. All calculated LCST's are included in Table 1, and the values for the n-alkanes between pentane and tridecane are compared with experimental values [2, 4, 14, 15] in Fig. 4. These results show that while the BGY lattice model with the parameters of Table 1 somewhat underestimates the LCST's for the shorter chains, it gives a very good description of the data for the higher alkanes.

The influence of the chain length of the polymer on its solubility is illustrated in Fig 5. The symbols indicate experimental data by Kodama and Swinton [4] for three polyethylene samples of different molecular masses in decane. We calculated the coexistence curves for polyethylene in decane for three comparable molecular masses (see Table 1) using the coexistence conditions Eqs. (12). Shown in Fig. 5, as a function of the mass fraction c, are the differences between the coexistence temperatures and the

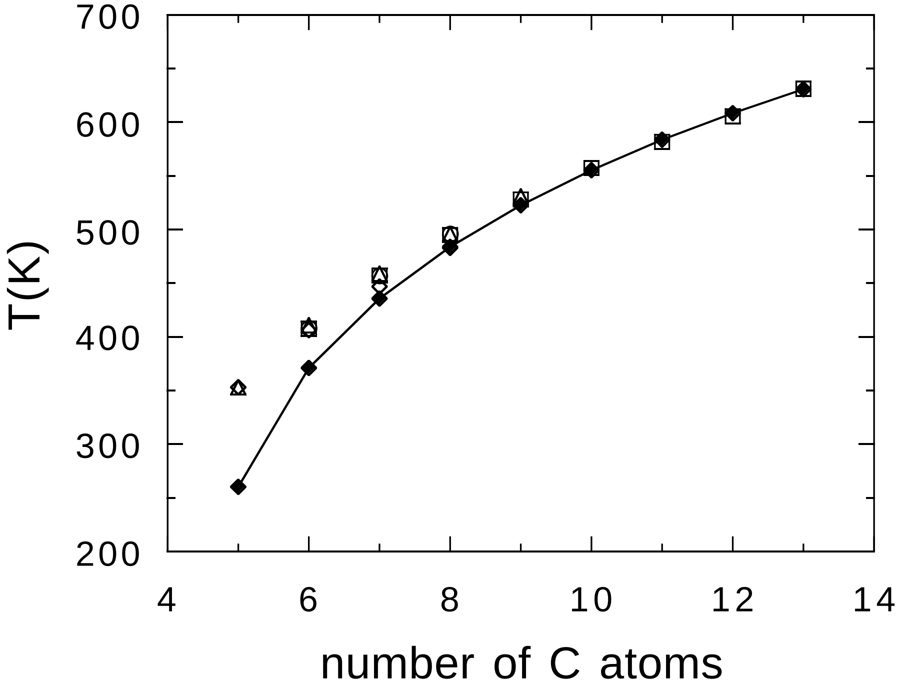

Figure 4: Lower critical solution temperatures for polyethylene in n-alkanes at $P =$ 0.1MPa. The symbols represent experimental data for Marlex-50 by Orwoll and Flory [2] (open circles), for Kodama and Swinton's [4] longest chain polymer PE Type 2 (open squares), extrapolated values to $M \to \infty$ by Hamada et al. [14] (open diamonds), and values collected by Charlet and Delmas [15] (open triangles). The filled diamonds on the solid line indicate values calculated with the aid of Eqns. (14) and (10) and the values presented in Table 1 together with Eqns. (15) and (16).

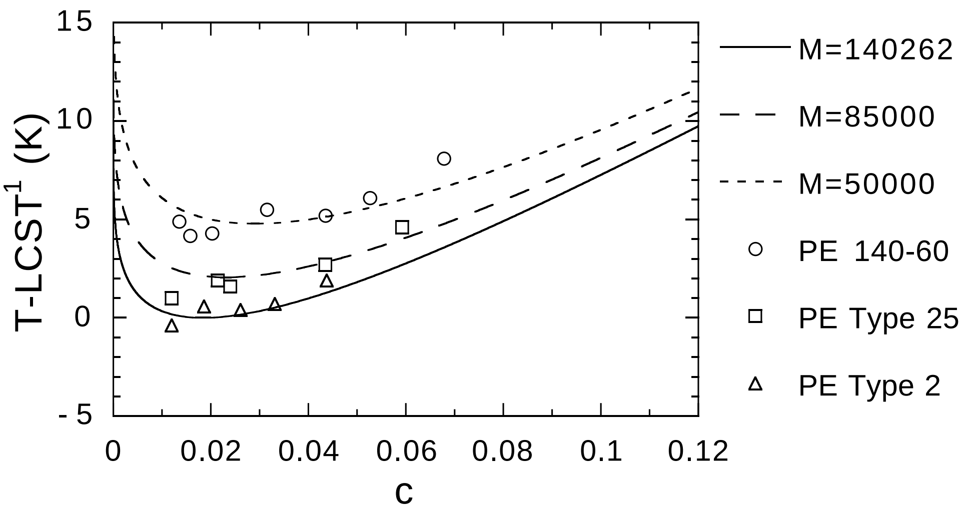

Figure 5: Coexistence curves for polyethylene in n-decane at $P = 0.1$MPa as a function of the mass fraction c. The symbols correspond to experimental data by Kodama and Swinton [4] the lines represent values calculated according to Eqn. (11) with the aid of the parameters in Table 1 and Eqns. (15) and (16). [1] For the experimental data, the LCST ($T = 557.6$K) of PE Type 2 has been subtracted from the coexistence temperatures, while the predicted LCST ($T = 555.7$K) of PE with molecular mass 140262 has been subtracted from the calculated values.

calculated and experimental values of the LCST of the longest chain, respectively. Since the experimental data in the paper by Kodama and Swinton [4] were not tabulated but presented in a graph the comparison is not exact. It appears, however, that the effect of changing molecular mass on the coexistence temperatures of polyethylene in decane is predicted well by the BGY lattice model.

Conclusion

With the aid of the system-dependent parameters for the pure components as well as the geometric mean approximation for the interaction energy, the BGY lattice model has been shown to predict LCST's for solutions of polyethylene in alkanes in very good agreement with experimental data. The theory also captures the effect of changing polymer molecular mass on solubility. In current work, we are investigating the influence on miscibility of polymer and solvent architecture.

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